X-RAY ORIENTATION INVESTIGATIONS ON NEOPRENE AND CELLULOSE MATERIALS

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INAUGURAL DISSERTATION

by

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X-ray orientation investigations on neoprene and cellulose materials

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These investigations comprise four papers previously published by the author. The papers have been given the reference numbers (1)–(4) and are listed below.

(1) Some X-ray experiments on the orientation properties of synthetic rubber of polychloroprene type. Arkiv Kemi *10*, 199 (1956).

(2) Some experiments concerning the effect of temperature on the crystallinity (orientation) in elongated neoprene specimens. Arkiv Kemi *11*, 57 (1957).

(3) Some notes on the intensity distribution along the X-ray interference circles for some simple types of orientation in polycrystalline specimens. Arkiv Kemi *12*, 9 (1958).

(4) X-ray orientation investigations on some Swedish cellulose materials. Arkiv Kemi *12*, 437 (1958).

In the present paper some examples of previously published orientation and crystallinity determinations from X-ray diffraction patterns are briefly mentioned and a short review is given of the methods applied for the papers (1–4) and of the results.

Examples of X-ray orientation and crystallinity investigations

The intensity distribution along an X-ray interference circle from a polycrystalline specimen, in which the crystallites are oriented in some way, offers a possibility to investigate the orientation properties of the material. This was first pointed out and the foundation for such investigations laid by Polanyi (16) in 1921. Since that time a very large number of orientation investigations has been published dealing with inorganic and organic materials of crystalline and semi-crystalline structure. Reviews and references are found in different textbooks, some examples of which are given in the references (5–14).

The following treatment will be limited to investigations of oriented semi-crystalline materials and only the "wide-angle" X-ray scattering and the photographic recording method will be discussed. A type of crystallite orientation which is often encountered with high polymeric materials is the fibre orientation which gives diagrams similar to those obtained by stretched rubber or by some oriented cellulose specimens, even if more complicated types of orientation are also found, e.g. in natural cellulose materials. Examples of fibre diagrams, obtained on plane films with the primary beam normal to the fibre axis, are easily found in the textbooks (e.g. (7)) and also in the papers (1) and (4) (cf. (1), Fig. 1, and (4), Fig. 7).

Stretched natural rubber and oriented cellulose are different with regard to the formation of the crystallites. In rubber (and rubberlike substances) which has not been frozen or stored for a long time crystallites are not present before stretching. When the material is elongated the crystallites are formed and oriented almost parallel with the direction of elongation. The X-ray diagram contains the superimposed diagrams of the crystalline, parallel oriented part of the material and of the amorphous and apparently unoriented part. For natural rubber the "crystalline" interference spots are clearly separated from the main "amorphous" ring, whereas for polychloroprene rubber the strongest "crystalline" spot falls on the ring. The relative intensities of the spots and the ring depend on the fraction of crystalline material in the specimen. In cellulose and many other high polymers (also frozen rubber) crystallites exist in unoriented specimens which give X-ray diagrams with a number of homogeneous Debye-Scherrer circles superimposed on the diagram of the amorphous part of the material. On orientation of the specimen intensity maxima appear on the circles. The width along the circle and relative intensity of these maxima depend upon the sharpness of orientation and upon the amount of oriented material.

The possibilities to obtain values, related to the orientation properties, from fibre diagrams or similar diagrams from rotationally oriented specimens are somewhat different depending upon the appearance of the diagram. For the diagrams obtained from stretched rubber materials, where the sharpness of orientation is practically constant but the intensity of the interference spots varies, measurements of this variation are a natural way to gain information regarding the fraction of crystalline and oriented material in such substances. Determinations of this kind were first reported by Hauser and Mark (16) who measured the intensity of the different interference spots in diagrams of stretched natural rubber in relation to the maximum intensity obtainable for each spot. Another method to measure the intensity of the interference spots has been used by Clark *et al.* (17) who used a Ni-interference recorded on the same film as the rubber diagram as intensity reference. The two papers mentioned above are examples of investigations where intensity measurements have been used to give relative values of the amount of crystalline material in the specimen.

Experiments to obtain absolute values of the crystallinity in stretched specimens of natural rubber have been made by Field (18) who measured the intensity of the amorphous ring in the diagrams of stretched rubber. The intensity of the amorphous ring for unstretched specimens of known thickness was used for calibration and corrections for differences in the exposure were applied. The absolute crystallinity in rubber samples has also been determined by Goppel and Arlman ((19, 20) reviewed in (13)) who utilized a more refined method. According to this method the intensities are determined from radial microphotometer recordings and as intensity standard are used interference circles from an inorganic substance recorded near the center of the rubber interference diagrams.

Orientations of higher order in rubber specimens have been studied by Gehman and Field (21) by measurements of the intensities of different interference spots.

For materials, e.g. cellulose, which may show differences both in the type and the sharpness of orientation and in the crystallinity, the X-ray diagram permits determinations of values both for the orientation and for the crystallinity. Many of the investigations of the type and sharpness of orientation are based on determinations of the intensity distribution along a strong interference circle (for cellulose often the circle corresponding to the (002)-plane). Such measurements on cellulose materials

were published by Sisson and Clark (22) in 1933 and later by several authors (also on other materials) to whom references are given in the textbooks (e.g. (8, 10, 12)).

Intensity distributions for spirally oriented specimens were given in (22) and by Sisson (23) who also in a later investigation (24) discussed and classified the different types of crystallite orientations and among them orientations of higher order.

From 1933 and onwards some important investigations on the subject of deformation and orientation of materials with fibre molecules were also published by Kratky *et al.* In a paper (25) Kratky discussed the orientation caused by stretching a swollen film containing crystallites and gave a method to calculate the intensity distribution for interference circles corresponding to planes normal to the direction of stretching (diatropic planes) and to planes parallel to that direction (paratropic planes). An experimental method to determine the intensity distribution for an interference circle from a series of radial microphotometer curves was discussed in reference (26). Other investigations on the deformation mechanism in fibre materials are found in (8). In a paper by J. J. Hermans *et al.* (27) intensity distribution investigations based upon Kratky's work (25) were again discussed and an equation was given for the calculation of the intensity distribution for an arbitrary plane from the intensity distribution of a diatropic plane. A treatise of fibre and spiral orientations has also been given by Matano (28) and a further development from (25) by Kratky *et al.* (29).

In most of the X-ray works on orientation properties a parameter to characterize the orientation is derived in some way from the width of the peak of the intensity distribution along an interference circle. One possibility and perhaps the simplest is to calculate the width in angular measure at half the maximum height. P. H. Hermans *et al.* have derived a more elaborate expression for an X-ray orientation factor based upon measurements on the intensity distribution curves (reviewed in (8)).

X-ray determinations of the fraction of crystalline material in cellulose and other semi-crystalline high polymers are a more complicated problem than crystallinity determinations in rubberlike materials, which can be obtained in a non-crystalline state. One of the latest contributions to this field has been given by P. H. Hermans and Weidinger ((30) and later papers) who have developed a method utilizing an experimental technique similar to that used by Goppel. Their method can be used both for relative and absolute measurements of the crystallinity.

All the investigations mentioned above have been made with the photographic recording method but it should be noted that the Geiger counter method has been introduced (31) for orientation and crystallinity measurements.

Methods applied in the papers (1–4)

The aim of this work was primarily an investigation of different preparations of neoprene, something like the investigation by Field (18) on natural rubber. It was desirable that the method applied should permit a comparatively simple determination of a relative parameter for the orientation. Absolute determinations were not attempted.

First the orientation of elongated neoprene specimens was investigated (1). Qualitatively it is easily understood that the area of the peaks, which are obtained for the intensity distribution along the strongest interference circle, is a relative measure of the amount of oriented crystallites in the specimen (see (1), Fig. 6). By applying the mode of calculation used by Kratky *et al.* (25, 27) it is possible to derive an

expression which under certain conditions gives the fraction of oriented material as a function of the area of the peaks and the total area under the intensity distribution curve (1). The most important condition is that both the oriented and the non-oriented material, scattering to the circle investigated, must have the same scattering power, i.e. the same degree of crystallinity, which probably cannot be fulfilled for neoprene. Hence a value for the oriented material obtained in this way can only be a relative value. As the peaks are due to crystallites formed on stretching, the value obtained is also a relative measure of the crystallinity in the specimen. By measurements of the specimen thickness and by comparing the difference between the total area under the microphotometer curve and the peak area, with the areas for unstretched specimens of known thickness (cf. (18, 19)), it should be possible to get absolute values but the procedure would be more laborious. Some other circumstances (background determination and integration over the radial breadth of the circle) which have been mentioned (1) also would cause difficulties in absolute determinations.

The value chosen as a relative measure of the crystallinity was simply the quotient between the area of the peaks and the total area under the microphotometer curve along the interference circle. The exposure and developing conditions for the film were kept as constant as possible but corrections for differences in these factors were not applied. Corrections in this respect could only have been made with the aid of blackening curves which again would have increased the experimental work. It is also seen that differences in the exposure are partly compensated because both the area of the peaks and the total area are influenced. Besides the relative crystallinity value, the breadth of the peaks at half the maximum height was measured.

The measurements of the orientation (or crystallinity) as a function of the temperature of elongated neoprene specimens (2) could have been made with the same method as for the orientation-elongation experiments. This was also attempted at the beginning but, as it was found possible to use the continuous recording method described (2), this latter was applied for the experiments. In this method only the intensities at three points were recorded on the film which was moved in a synchronous way with the change (increase) of the temperature. The points recorded were the maximum on the interference circle, one point on the circle, in the middle between the equator and the pole, and one background point. The change of the crystallinity was measured directly on the microphotometer recordings of the traces of the spots recorded on the film and a crystallinity–temperature curve (a kind of melting curve) was drawn. As in the previous experiments the conditions were kept as constant as possible and no corrections for the exposure were applied. Obviously under these conditions only a relative measure for the crystallinity could be obtained. Only the temperatures at some characteristic points (which were not always obtained) of the crystallinity–temperature curve were determined but the crystallinity values were not considered. It is possible that the shape of the curve changed slightly with the exposure. A scattering of the temperature values at the beginning of the melting and of an inflexion point of the curve can be interpreted in that way. However, for those cases where a final "melting point" was obtained this was reproduced quite well. Of course a method like this is in many respects inferior to a method giving absolute crystallinity values, but the continuous recording procedure saves considerable time which in many cases is a great advantage.

When the crystallinity determination of stretched neoprene specimens seemed to give a reasonable result some experiments were also made with wood specimens (4).

The experimental method was the same as for neoprene and the same values were measured. With wood and other cellulose materials the area quotient is, of course, related to the amount of oriented material and not (or at least only slightly) to the crystallinity.

In the case of wood the orientation may be rather complicated because of the differently oriented layers in the wood tracheids and because of the spiral structures which are not seldom encountered. To gain a better understanding of the situation and to facilitate the interpretation of the X-ray diagrams, an attempt was made to extend the calculations made by Kratky (25) and by J. J. Hermans *et al.* (27) to more general cases (3). For this purpose the approach used by the authors mentioned was again applied, but the calculations were carried through in a different way.

Summary of the results

Theoretical

In (1) an expression ((1), Eq. (12)) has been derived which, for a partly oriented rotationally symmetric specimen, gives the fraction of oriented material as a function of the area of the peaks and of the total area under the intensity distribution curve for an interference circle corresponding to a plane oriented parallel to the fibre axis.

In (3) an integral equation ((3), Eq. (6)) has been derived which, for an oriented, rotationally symmetric specimen, connects a frequency function, related to the intensity distribution along the interference circle for a plane parallel to the specimen axis, with a similar frequency function for an arbitrary plane. To permit the calculation of intensity distribution curves for arbitrary planes the integral equation had to be solved for a special case. This has not been done exactly but an approximate solution related to the frequency function for a plane oriented parallel to the specimen axis has been found. Utilizing this approximate solution, frequency functions for some planes in a fibre oriented specimen have been numerically calculated and checked according to a normalizing condition imposed upon the frequency functions.

The equation derived and a similar approximation as above were also tried numerically for a simple case of higher order orientation (3), for two planes normal to each other and parallel to the specimen axis. For the case investigated the calculations gave a fairly good agreement with a theoretical curve.

For the simplest case of spiral structure (a spirally wound fibre) an expression ((3), Eq. (19)) for a frequency function related to the spiral has been derived for a plane which, in the spirally wound fibre, is oriented parallel to the fibre axis. Utilizing this expression numerical calculations for a special case have been made and checked to fulfill the normalizing condition.

Experimental

A method has been derived (1) for the determination of relative orientation and in some cases crystallinity values. For neoprene samples relative values of the crystallinity have been determined at different elongations and elongation–crystallinity curves have been plotted (1). These curves are similar to corresponding curves obtained for natural rubber (18).

For investigation of the decrease in crystallinity (relative value) of elongated neoprene with increasing temperature (i.e. a "melting" process) a continuous re-

cording apparatus has been developed (2) and used for different neoprene samples under conditions of constant elongation and constant load (2). At constant elongation a reproducible "melting point" was obtained with unvulcanized specimens. For different materials temperatures from 45°C to 56°C were found. "Melting points" were not always obtained with vulcanized materials, but a series of vulcanized specimens of the same composition but with different curing times gave "melting points" which seemed to be in relation to the curing times. The normal curing time (45 min.) corresponded to a "melting" at about 50°C. In the experiments at constant load the specimens were elongated by the load as the temperature was increased. The crystallinity did not change much during heating and no "melting points" were obtained.

The method used for the relative crystallinity determinations of neoprene was also applied for relative orientation determinations of Swedish spruce (*Picea excelsa*) (4). The breadth of the peaks at half the maximum height was also determined as a measure of the sharpness of orientation. Three different trees giving examples of normal wood and of compression wood were investigated. In one of the trunks a number of successive annual rings in a radius of a cross-section were investigated. In this case there seemed to be a relation between the relative value of the orientation and the half maximum breadth and between the orientation value and the thickness of the annual rings.

The X-ray diagrams (4) gave a general picture which agreed with the results reported from investigations of other wood materials. However, a comparatively large number of the diagrams of normal wood were very well defined, and in this respect the material investigated may be different from most other wood materials.

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